



COATING COMPOSITION

BACKGROUND OF THE INVENTION

5 This application is a continuation-in-part application of Serial No. 09/763,927, filed February 26, 2001, the contents of which are hereby incorporated herein by reference.

Field of the Invention

10 The present invention relates to coating compositions useful for forming protective films with which smooth and transparent surfaces can be obtained. More particularly, the present invention relates to coating compositions useful for forming protective films on color filters that have been formed
15 on top of glass or transparent materials.

Background Art

In recent years, liquid crystal displays have been extensively used in audiovisual equipment, and electronic devices such as personal computers. In particular, the demand
20 for color displays is now rapidly increasing because they are excellent in visibility and amount of information. To produce color displays, color filters in the shape of, for instance, mosaic or stripes are usually formed on transparent substrates such as glass by, for example, a dyeing, printing, pigment
25 dispersing or electrodeposition process.

In general, these color filters are produced so that their thickness will become approximately 1 micron, where it is inevitable that the color filters have surface roughness in the submicron range. In color STN displays, this roughness affects
30 the quality of display (unevenness in color, etc.). In order to eliminate unevenness in display, it is necessary to make the surface roughness of the color filters 0.1 microns or less. To obtain such even surfaces, thermosetting acrylic resins have conventionally been applied to the surfaces of the color
35 filters.

Not only in liquid crystal display devices but also in charge coupled devices, the surfaces of color filters require protection. Protective films are herein needed to protect these color filters from severe conditions under which post-treatments
5 are conducted, for example, from solvents, acidic or alkaline solutions, etc. that are used for dipping treatment, and from high-temperature heat that is generated while electrode layers are formed by sputtering. Such protective films are required to be smooth, strong, highly transparent, and excellent in
10 resistance to heat and chemicals, that is, not undergoing change in color and quality for a long period of time. To meet these requirements, thermosetting resins including epoxy copolymers have so far been used.

Conventionally-known many coating compositions for forming
15 protective films are of two-bottle type. In the case of two-bottle-type coating compositions, it is necessary to mix two liquids before use, and to immediately use the mixture once they are mixed. In addition, the coating compositions can produce, depending on their compositions, sublimates while they are
20 hardening; the sublimates are crystallized to give foreign particles, and these foreign particles can cause troubles during the production of liquid crystal panels. There have therefore been demanded coating compositions that never give crystallized materials.

25 Japanese Patent Laid-Open Publication No. 216307/1985 describes protective films made from glycidyl acrylate and polyhydric carboxylic anhydrides or acids. Agents for forming these protective films can be obtained as either one-bottle- or two-bottle-type coating compositions. In general, one-bottle-
30 type coating compositions are easy for use, but poor in storage stability. The above one-bottle-type coating compositions hardened and became unusable within about 1 month. It was also confirmed that films made from these one-bottle-type coating compositions were poor in adhesion, transparency and evenness as
35 compared with films made from the two-bottle-type coating compositions. On the other hand, coating compositions of two-

bottle type are, in general, excellent in storage stability, and can provide films having excellent adhesion and high transparency; however, it is necessary to mix two liquids before use, and the two liquids rapidly reacts with each other once
5 mixed. In the case of the above two-bottle-type coating compositions, it was necessary to use the mixture within 2 days after mixing two liquids.

SUMMARY OF THE INVENTION

10 We now found that coating compositions having high storage stability, capable of providing excellent protective films can be obtained by the combination use of specific polymers and crosslinking agents, and accomplished the present invention on the basis of this finding.

15 An object of the present invention is therefore to provide coating compositions that are essentially stable and that can provide excellent protective films.

Another object of the present invention is to provide one-bottle-type coating compositions that are easy for use, that are
20 excellent in storage stability, and that can provide protective films excellent in adhesion, transparency and evenness.

A coating composition according to the present invention comprises:

(A) at least one polymer containing carboxyl group, having
25 a weight-average molecular weight, calculated in terms of styrene, of 5,000 to 200,000, an acid value KOH of 10 to 200 mg/g, and a glass transition temperature of 50 to 250°C,

(B) a polyfunctional epoxide-group-containing compound having at least one benzene ring or 5-, 6-, or 7-membered
30 heterocycle ring containing at least one heteroatom selected from nitrogen, oxygen or sulfur or cyclohexyl group or combinations thereof, and two or more epoxy groups, serving as a crosslinking agent,

(C) a reaction accelerator, and

35 (D) an organic solvent.

DETAILED DESCRIPTION OF THE INVENTION

A coating composition according to the present invention contains at least (A) a polymer, (B) a crosslinking agent, (C) a reaction accelerator, and (D) a solvent.

5 (A) Polymer

In the present invention, the polymer (A) is defined as a polymer containing carboxyl group, having a weight-average molecular weight, calculated in terms of styrene, of 5,000 to 200,000, an acid value KOH of 10 to 200 mg/g, and a glass
10 transition temperature of 50 to 250°C. In a preferred embodiment of the present invention, the polymer has a weight-average molecular weight of approximately 10,000 to 100,000, and an acid value KOH of about 30 to 100 mg/g.

Further, in a preferred embodiment of the present
15 invention, the polymer can be dissolved or, at least, swelled in aqueous alkaline solutions.

Preferable examples of such polymers are copolymers of acrylic or methacrylic esters and aromatic vinyl compounds. Examples of acrylic or methacrylic esters include methyl
20 acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, ethylhexyl methacrylate and phenyl acrylate. Examples of aromatic vinyl compounds include styrene, α -methylstyrene and *p*-methylstyrene.

These copolymers may be of any type; they may be any of
25 random copolymers produced by addition polymerization, block copolymers, and the like. Further, there is no particular limitation on the copolymerization process, and any one of solution polymerization process, emulsion polymerization process, and the like can be adopted to produce the copolymers.

The amount of the polymer to be used in the present
30 invention may be properly established so that excellent protective films can be obtained. However, the amount of the polymer to be used is preferably about 5 to about 30% by weight, more preferably about 10 to about 25% by weight of the coating
35 composition.

The glass transition temperature of the polymer was determined using ASTM D3418, "Standard Test Method for Transition Temperatures of Polymer by Thermal Analysis."

(B) Crosslinking Agent

5 In the present invention, the crosslinking agent is a polyfunctional epoxide-group-containing compound having, in one molecule, at least one benzene ring or 5-, 6-, or 7-membered heterocycle ring containing at least one heteroatom selected from nitrogen, oxygen or sulfur or cyclohexyl group or
10 combinations thereof, and two or more epoxy groups. In one embodiment of the present invention, the epoxide-group-containing compound preferably has phenyl group and cyclohexyl group, more preferably at least two phenyl groups.

In a preferred embodiment of the present invention, the
15 epoxide-group-containing compound has three or more epoxy functional groups.

Specific examples of the crosslinking agent include bisphenol acetone diglycidyl ether, phenol novolak epoxy resins, cresol novolak epoxy resins, triglycidyl isocyanurate,
20 tetraglycidyl-diaminodiphenylene, tetraglycidyl-m-xylenediamine, tetraglycidyl-1,3-bis(aminoethyl)cyclohexane, 1,1,2,2-tetraphenylolthane tetraglycidyl ether (tetraphenyl-glycidyl ether ethane), triphenylolthane triglycidyl ether (triphenylglycidyl ether ethane), triphenylolmethane triglycidyl
25 ether, bisphenol hexafluoro-acetodiglycidyl ether, 1,3-bis(1-(2,3-epoxypropoxy)-1-trifluoromethyl-2,2,2-trifluoromethyl)benzene, 4,4-bis(2,3-epoxypropoxy)octafluorobiphenyl, triglycidyl-p-aminophenol, tetraglycidyl-m-xylenediamine, 2-(4-(2,3-epoxypropoxy)phenyl)-2-
30 (4-(1,1-bis(4-(2,3-epoxypropoxy)phenyl)ethyl)phenyl)-propane, and 1,3-bis(4-(1-(4-(2,3-epoxypropoxy)phenyl)-1-(4-(1-(4-(2,3-epoxypropoxy)phenyl)-1-methylethyl)phenyl)ethoxy)-2-propanol.

In the present invention, the crosslinking agent may be
35 used in any amount. It is however preferable to use the

crosslinking agent in an amount of about 1 to about 50 parts by weight, more preferably from about 5 to about 30 parts by weight for 100 parts by weight of the polymer.

(C) Reaction Accelerator

5 In the present invention, any compound can be used as the reaction accelerator as long as it accelerates the reaction between the carboxyl group contained in the polymer and the epoxide group contained in the crosslinking agent. In one embodiment of the present invention, an isocyanate or amine
10 compound is preferably used as the reaction accelerator; and a blocked isocyanate, tertiary amine or blocked amine compound is more preferably used. Preferable examples of blocked isocyanates include hexamethylenediisocyanate blocked by phenol. Preferable
15 examples of blocked amines include hexamethylenediamine carbamate. The amount of the reaction accelerator to be added is preferably about 0.1 to 10 parts by weight for 100 parts by weight of the polymer.

(D) Solvent

20 In the present invention, an organic solvent is used to dissolve therein the above-described polymer and crosslinking agent. In a preferred embodiment of the present invention, the organic solvent is selected from the group consisting of propylene glycol-based, ethylene glycol-based, lactic acid-
25 based, butyric acid-based, acetic acid-based, formic acid-based, and γ -butyrolactone solvents, and mixtures thereof. When any of these organic solvents is used, the resulting coating composition is stable over approximately 6 months after preparation, and can provide a uniform coating film having no
30 unevenness in coating. It is thus possible to obtain protective films that are excellent in adhesion, evenness, transparency, durability, and resistance to abrasion, stains and chemicals.

 Specific examples of the organic solvent for use in the present invention include glycol ether and acetate-based
35 solvents such as propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol propyl ether, propylene glycol t-

butyl ether, dipropylene glycol methyl ether, dipropylene glycol propyl ether, tripropylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether acetate, ethylene glycol ethyl ether, ethylene glycol methyl ether, 5 ethylene glycol butyl ether, ethylene glycol isopropyl ether, ethylene glycol n-butyl ether, cellosolve acetate, methyl cellosolve acetate, ethyl cellosolve acetate, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, diethylene glycol dimethyl ether, diethylene glycol 10 diethyl ether, diethylene glycol monoacetate, diethylene glycol monoethyl ether acetate, propylene glycol phenyl ether, propylene glycol ethyl ether acetate, triethylene glycol butyl ether, 3-methyl-3-methoxybutyl acetate, and 3-methyl-3-methoxybutanol; lactic acid-based solvents such as ethyl 15 lactate, methyl lactate, butyl lactate and pentyl lactate; acetic acid-based solvents such as butyl acetate, amyl formate, isoamyl acetate, isobutyl acetate, methoxybutyl acetate, and butyl propionate; and butyric acid-based solvents such as isobutyl butyrate, butyl butyrate and ethyl pyruvate.

20 In a preferred embodiment of the present invention, propylene glycol methyl ether acetate, or an organic solvent mixture consisting of propylene glycol methyl ether acetate and other organic solvents is used as the organic solvent. Preferable examples of organic solvents that can be used 25 together with propylene glycol methyl ether acetate include propylene glycol-based, ethylene glycol-based, lactic acid-based, butyric acid-based, acetic acid-based, formic acid-based, and γ -butyrolactone solvents, and mixtures thereof.

The amount of the organic solvent to be used may properly 30 be adjusted depending upon the concentration of the polymer, crosslinking agent and reaction accelerator in the coating composition; for example, this amount is about 45 to 95% by weight of the coating composition.

Formation of Protective Film

35 The coating composition according to the present invention is applied to a substrate to form thereon a protective film.

Therefore, in another aspect of the present invention, a process for producing a substrate comprising a protective film is provided. This process comprises applying the coating composition of the present invention to a substrate to form thereon a protective film. A further aspect of the present invention relates to the use of the coating composition of the present invention for the production of a substrate comprising a protective film.

Non-limitative examples of substrates to which the coating composition of the present invention can be applied include color filters, glass, glass filters, black matrixes, and substrates made from a variety of polymers (polyimide, polyamide, polyethylene, acrylic resins, etc.), indium titanium oxide, silicon nitride, metallic oxides (titanium oxide, silicon oxide, chrome oxide, etc.), or metals (aluminum, copper, etc.).

The substrate covered with a protective film made from the coating composition of the present invention can be used, for instance, semiconductors, flat panel displays, and electronic devices.

To form the protective film, the coating composition according to the present invention is applied to the above-described substrate, and then hardened by heating.

Any coating method can be adopted to apply the coating composition of the invention; and a spin, roll or spray coating method, for instance, can be employed. A spin coating method is, above all, preferred because a uniform film can readily be obtained by this method.

The conditions under which the coating composition applied is hardened may properly be established by taking the type of the polymer, the composition of the coating composition, etc. into consideration. For instance, the coating composition applied may be hardened at a temperature of 150 to 270°C for a time period of about 20 minutes to 10 hours.

EXAMPLES

The present invention will now be explained more specifically by referring to the following examples. However,

the present invention is not limited to or limited by these examples in any way.

(a) Preparation of Coating Composition

A coating composition was prepared in the following manner.

5 First of all, a first mixture was obtained by mixing the below-described polymer, crosslinking agent, and reaction accelerator. To this mixture was added a mixture of solvents, the mixing ratio by weight of the solvents being as shown below, thereby obtaining a coating composition containing 17% by weight of the
10 first mixture.

Example 1

Polymer I	89 g
(methacrylic acid-styrene copolymer, weight-average molecular weight: approx. 15,000, 15 acid value: 55 mg/g)	
Triphenylolethane triglycidyl ether	10.g
Blocked hexamethylenediisocyanate	1 g
Propylene glycol methyl ether acetate	50%
Ethylene glycol monoethyl ether acetate	50%

20 Example 2

Polymer I	89 g
Triphenylolethane triglycidyl ether	10.g
Blocked hexamethylenediisocyanate	1 g
Propylene glycol methyl ether acetate	50%
25 Diethylene glycol monoethyl ether	50%

Example 3

Polymer I	89 g
2-(4-(2,3-Epoxypropoxy)phenyl)- 2-(4-(1,1-bis(4-(2,3-epoxypropoxy)- 30 phenyl)ethyl)phenyl)propane	10 g
Blocked hexamethylenediisocyanate	1 g
Propylene glycol methyl ether acetate	50%
Ethylene glycol monoethyl ether acetate	50%

Example 4

35 Polymer I	89 g
2-(4-(2,3-Epoxypropoxy)phenyl)-	

	2-(4-(1,1-bis(4-(2,3-epoxypropoxy)-phenyl)ethyl)phenyl)propane	10 g
	Blocked hexamethylenediisocyanate	1 g
	Propylene glycol methyl ether acetate	50%
5	Diethylene glycol monoethyl ether	50%

Example 5

	Polymer I	89 g
	1,3-bis(4-(1-(4-(2,3-epoxypropoxy)phenyl)-1-(4-(1-(4-(2,3-epoxypropoxyphenyl)-1-methyl-ethyl)phenyl)ethyl)phenoxy)-2-propanol	10 g
10	Blocked hexamethylenediisocyanate	1 g
	Propylene glycol methyl ether acetate	50%
	Ethylene glycol monoethyl ether acetate	50%

Example 6

15	Polymer I	89 g
	1,3-bis(4-(1-(4-(2,3-epoxypropoxy)phenyl)-1-(4-(1-(4-(2,3-epoxypropoxyphenyl)-1-methyl-ethyl)phenyl)ethyl)phenoxy)-2-propanol	10 g
	Blocked hexamethylenediisocyanate	1 g
20	Propylene glycol methyl ether acetate	50%
	Diethylene glycol monoethyl ether	50%

Example 7

	Polymer I	89 g
	1,3-bis(1-(2,3-epoxypropoxy)-1-trifluoro-methyl-2,2,2-trifluoromethyl)benzene	10 g
25	Blocked hexamethylenediisocyanate	1 g
	Propylene glycol methyl ether acetate	50%
	Ethylene glycol monoethyl ether acetate	50%

Example 8

30	Polymer I	89 g
	1,3-bis(1-(2,3-epoxypropoxy)-1-trifluoro-methyl-2,2,2-trifluoromethyl)benzene	10 g
	Blocked hexamethylenediisocyanate	1 g
	Propylene glycol methyl ether acetate	50%
35	Diethylene glycol monoethyl ether	50%

Example 9

	Polymer II	89 g
	(methacrylic acid-styrene copolymer, weight-average molecular weight: 41,000, acid value: 85 mg/g)	
5	1,3-bis(4-(1-(4-(2,3-epoxypropoxy)phenyl)-1-(4-(1-(4-(2,3-epoxypropoxyphenyl)-1-methyl-ethyl)phenyl)ethyl)phenoxy)-2-propanol	10 g
	Blocked hexamethylenediisocyanate	1 g
	Propylene glycol methyl ether acetate	50%
10	Diethylene glycol monoethyl ether	50%

Example 10

	Polymer II	89 g
	1,3-bis(1-(2,3-epoxypropoxy)-1-trifluoro-methyl-2,2,2-trifluoromethyl)benzene	10 g
15	Blocked hexamethylenediisocyanate	1 g
	Propylene glycol methyl ether acetate	50%
	Ethylene glycol monoethyl ether acetate	50%

(b) Formation of Protective Film

A 1.2- μ m color filter serving as a substrate was spin-coated with the above-obtained coating composition at a rotational speed of 1,000 rpm/5 seconds, and placed on a hot plate at 110°C for 1 minute for drying. The coating composition thus dried was then subjected to thermal hardening at a temperature of 250°C for 1 hour on a hot plate.

(c) Tests for Evaluating the Properties of Protective Film

The above-obtained protective film was subjected to the following evaluation tests.

Evaluation 1: Evenness

The thickness of the protective film was measured to determine the average film thickness, and the standard deviation of film thickness.

Evaluation 2: Adhesion

The substrate covered with the protective film was left in a high-temperature (80°C) high-humidity (95 RH%) environment for 100 hours. The substrate was then withdrawn from this environment, and square notches were made on the protective film

with a knife. A peeling test using an adhesive tape was conducted on this notched protective film.

Evaluation 3: Measurement of Transmittance

5 The transmittance of the protective film was measured by a conventional method.

Evaluation 4: Abrasion Resistance

The hardness of the protective film was measured by means of a pencil hardness tester that meets the JIS requirements.

Evaluation 5: Chemical Resistance

10 1-mm square notches were made on the protective film formed on the substrate. This substrate was immersed in NMP (n-methylpyrrolidone) or acetone for 1 hour, and the conditions of the protective film were visually observed.

The results of the above-described evaluation tests were as
15 shown in the following table.

Table

	1. Evenness		2. Adhesion	3. Transmittance	4. Surface Hardness	5. Chemical Resistance	6. Storage Stability	
	Average Film Thickness	Standard Deviation of Film Thickness					1 month	6 months
Ex. 1	1.5 μm	0.12 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 2	1.8 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 3	1.7 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 4	1.9 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 5	1.7 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 6	1.9 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 7	1.8 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 8	2.1 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 9	1.8 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O
Ex. 10	2.1 μm	0.15 μm	Caused no Peeling	98% or more	>4H	Observed no peeling or the like	O	O